Status and Trends of Brominated Flame Retardants in the South China Coastal Region with Special Reference to Marine Cetaceans and Waterbird Eggs

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Introduction

South China is one of the most rapidly-growing regions in the world. The Pearl River Delta (PRD), located in Guangdong Province, has been subject to intense economic and industrial activities since 1980 and has become the leading industrial and economic centre in the area. Situated at the mouth of the Pearl River, Hong Kong receives persistent toxic contaminants into its marine habitats from a variety of anthropogenic sources (Lam et al. 2008). Located east of Guangdong Province, Fujian is another economically developing province in South China; Xiamen and Quanzhou are two important port cities in the province. Xiamen was designated as a Special Economic Zone in 1986, while Quanzhou started large-scale industrial activities in 1991. The coastal environment of both cities has been undergoing strong modification due to rapid urbanization. While there are some data on heavy metals and certain traditional persistent organic pollutants (POPs) in environmental samples from the three coastal cities (Lam et al. 2008 and references therein; Lam et al. 2009), information on emerging chemicals of concern such as brominated flame retardants (BFRs) is limited.

Increasing concerns have been raised regarding these flame retardant products due to their persistence, bioaccumulative characteristics and potential adverse effects (Ruan et al. 2009). The penta-and octa-brominated diphenyl ether (penta-BDE and octa-BDE, respectively) commercial mixtures have been listed as POPs under the Stockholm Convention (UNEP 2009). Stringent regulations on PBDE use have led to the emergence of substitute chemicals, one group of which is the hexabromocyclododecanes (HBCDs). The presence of HBCDs has been reported in various environmental matrices at levels comparable to those of PBDEs (Covaci et al. 2006). In addition to HBCDs, novel halogenated flame retardants such as hexachlorocyclopentadienyldibromocyclooctane (HCDBCO) (Zhu et al. 2008) and 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and *bis*-(2-ethylhexyl)-tetrabromophthalate (TBPH), found in the commercial flame retardant mixture Firemaster® 550 (FM 550), have been detected in house dust in the US (Stapleton et al. 2008).

This paper describes the status of PBDE contamination in the eggs of two species of waterbirds, little egrets (*Egretta garzetta*) and black-crowned night herons (*Nycticorax nycticorax*), from Hong Kong, Xiamen and Quanzhou, and temporal trends in PBDE and HBCD concentrations as well as quantification of HCDBCO, TBB and TBPH in the Indo-Pacific humpback dolphin (*Sousa chinensis*) and finless porpoise (*Neophocaena phocaenoides*), the two resident cetacean species in Hong Kong. The dolphin is generally restricted to the northwestern waters of Hong Kong adjacent to the mouth of the Pearl River, whereas the porpoise is found in eastern waters. Both waterbirds and cetaceans are top predators which have been the subjects of previous monitoring studies.

Materials and Methods

Sample collection and preparation

Eggs of little egrets (LE) and black-crowned night herons (NH) were collected from Hong Kong, Xiamen and Quanzhou (n=5 for each species from each location) in 2004. Blubber samples of stranded Indo-Pacific humpback dolphins (n=17) and finless porpoises (n=33) were collected in Hong Kong between 2002 and 2007 and between 2003 and 2008, respectively. All the samples were stored at -20°C. Analysis of PBDEs and HBCDs followed previously established methods (Isobe et al. 2007; Lam et al. 2008) with modifications. Procedures for sample preparation for HCDBCO, TBB and TBPH analysis were similar to those for the analysis of PBDEs with some modifications.

Chemical analysis

Quantification of PBDEs was performed using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975c) for mono- to deca-BDE, using electron impact mode. Fourteen major PBDE congeners were quantified using the isotope dilution method to their corresponding $^{13}C_{12}$-labeled congeners. Quantification of HBCDs was carried out using an Agilent HP1100 liquid chromatograph coupled with an Applied Biosystems API 2000 triple quadrupole tandem mass spectrometer equipped with a Turbo IonSpray source operated in negative mode. Identification and quantification of HCDBCO, TBB and TBPH was conducted using a GC (Agilent 7890A) equipped with a mass-selective detector (Agilent 5975C) operated in electron capture negative ionization mode, similar to the analysis carried out by Stapleton et al. (2008) with some modifications. Concentrations of various flame retardants were expressed as ng/g lipid weight (lw).

QA/QC

Recoveries of $^{13}C_{12}$-labeled HBCDs and PBDEs in all samples were within 60-120% and recoveries of spiked HCDBCO, TBB and TBPH ranged from 70-120%. The efficiencies of Soxhlet extraction and clean-up procedures were checked prior to the chemical analysis and the recovery rates of $^{13}C_{12}$-labeled standards ranged between 70-120% (n=5). Procedural blanks were analyzed simultaneously with every batch of five samples to check for potential interferences or contamination and instrumental detection limits (IDLs) were estimated as the average signal of the blanks plus three times the standard deviation of the signals of the blanks.

Statistical analysis

Concentration comparisons were conducted by Student's t-tests if the data passed normality and equal variance tests; nonparametric Mann-Whitney Rank Sum tests were used otherwise (SigmaStat 3.5). Yearly median concentrations were used to perform log-linear regression for the whole monitoring dataset for dolphins from 1997-2007 and porpoises from 2000-2008, including data from 1997 to 2001 that was previously reported (Isobe et al. 2007). A three-year moving average smoothing function was fitted to the annual median concentrations to investigate possible non-linear trend components and was tested by means of ANOVA. Statistical analysis was conducted using Prism 2.01 and SigmaStat 3.5. Statistical significance was accepted at $p < 0.05$.

Results and Discussion

Spatial variation of PBDE concentrations and congener profile in waterbird eggs

Levels of total PBDEs detected in Hong Kong waterbird egg samples (LE: 140-760 ng/g lw; NH: 190-1000 ng/g lw) were generally higher than those of Xiamen (LE: 30-55 ng/g lw; NH: 54-200 ng/g lw) and Quanzhou (LE: 140-320 ng/g lw; NH: 240-380 ng/g lw), although only the difference between the samples from Hong Kong and Xiamen was statistically significant. The observed spatial variation may be attributed to differences in the quantities of BFRs used in the different locations, possibly reflecting the dissimilar industrial developmental phases among the three cities. LE and NH eggs from the same location had similar congeneric profiles. To facilitate inter-site comparison, data from the LE and the NH were pooled together. BDE47 was the most abundant congener in the samples from Hong Kong (9.2-320 ng/g lw) and Quanzhou (53-170 ng/g lw). However, BDE47 (7.0-49 ng/g lw) and BDE154 (8.6-68 ng/g lw) co-dominated the congener profile in the samples from Xiamen (Lam et al. 2007). Detection of BDE209 in egg samples from all three cities indicated its widespread occurrence in the coastal region of South China (Hong Kong: <0.5-59 ng/g lw; Xiamen: <0.5-5.2 ng/g lw; Quanzhou: 0.88-2.3 ng/g lw) (Lam et al. 2007).

Concentrations of various flame retardants and temporal trends of PBDE and HBCDs in cetaceans

All 50 cetacean blubber samples contained HBCDs, with concentrations ranging from 32 to 519 and from 4.1 to 501 ng/g lw for Indo-Pacific humpback dolphins and finless porpoises, respectively. α-HBCD dominated the isomer pattern in all samples analyzed. β- and γ-HBCD were detected in 54% and 60% of all samples, respectively. Mean concentrations of total PBDEs ranged from 1113 to 3590 ng/g lw in the two species, and were approximately one order of magnitude greater than the levels of total HBCDs measured in blubber samples. TBPH was detected in approximately 40% of samples, the majority of which were from porpoises. TBB was detected in 12% of samples at levels varying from IDL to 70 ng/g lw and all of the detectable samples were from porpoises. This is the first study to report TBB and TBPH in marine mammals. HCDBCO was undetectable in all of the samples. Significantly higher levels of HBCDs and PBDEs were found in dolphins than in porpoises, suggesting that the northwestern waters of Hong Kong are more contaminated by HBCDs and PBDEs than the eastern waters. In contrast, TBB and TBPH were mostly detected in porpoise samples, indicating the possible presence of a source of these new flame retardants in their habitat. No significant temporal trends in total PBDE concentrations in dolphins and porpoises were observed from 1997 to 2008, as tested by log-linear regression and three-year moving averages. However, between-year variation of PBDEs exhibited similar patterns between dolphins and porpoises, with peak concentrations occurring in 2003-2004 followed by relatively steady levels after 2006 (Lam et al. 2009). This observation could be partly explained by effective regulation and control of PBDE usage in countries around the world. Concentrations of total HBCDs, in contrast, showed a positive temporal trend in dolphin samples when log-linear regression analysis of yearly median concentrations was used (Pearson $r = 0.67$, $p = 0.047$), while the temporal trend in porpoises was not significant when tested by log-linear regression or three-year moving averages (Lam et al. 2009). The linear regression equation obtained for dolphins ($y = 0.090x + 1.6$) indicated that total HBCD concentrations would double from 1997 to 2017, assuming a constant rate of HBCD usage and release. The elevated trends of HBCDs observed in dolphins but not in porpoises could be due to the higher contaminant exposure levels in the northwestern waters of Hong Kong compared to the eastern waters.

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